HIGH DENSITY URANIUM SILICIDE WITH EXCESS URANIUM

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ABSTRACT

An experiment to prepare higher density fuel based on uranium silicide using excess uranium has been carried out. The weight percentage of uranium in the melt was chosen to exceed that of U in U_3Si_2 thus resulting in an ingot density of approximately 15.5 Mg/m^3. The melt of uranium and silicon was quenched and the ingot so obtained was pulverized and fabricated into fuel plates with aluminum powder as the matrix material and with aluminum alloy as the cladding material. Excess uranium metallic is known to have poor behaviour under irradiation. However, when suitable heat treatment is applied to the fuel plates this uranium will react with the aluminum matrix to form irradiation-stable UAl_x. The formation of UAl_x from the excess uranium and aluminum matrix has been found to take place at hot-rolling temperatures of fuel plates, i.e., in between 450 and 550°C, for an extended period of heating time. The higher the annealing temperature, the shorter the annealing time required for reaction. By ultimately having UAl_x in the meat of the fuel plates, replacing the metallic uranium, one can get rid of the undesirable irradiation behaviour of uranium while achieving the purpose of having higher uranium loading in the fuel plates. A simple calculation considering the amount of matrix material available for alloying reaction with free uranium in the dispersion shows that a dispersion fuel meat using this new fuel can reach a loading density between 6 and 7 MgU/m^3.

INTRODUCTION

The Reduced Enrichment for Research and Test Reactors (RERTR) Program initiated by the USA in 1978 has one of the main purposes to develop high density fuel which enable the replacement of HEU fuel in research reactors with LEU[1]. In 1988 the Program succeeded in licensing U_3Si_2 fuel as a new fuel for dispersion type fuel element capable of reaching a loading density of 4.8 MgU/m^3 [2]. Such a high loading density, however is not adequate to convert some reactors from using HEU into using LEU without significant operational neutronic penalty. This challenge leads to efforts to find higher density fuels. BATAN has set up RERTR-related program since 1988 with respect to the development of new fuel, especially uranium silicide [3].

In the case of hypostoichiometric U_3Si_2 fuel, solidification of an U-Si melt results in excess uranium that exists in solid form between the dendrites of U_3Si_2, the amount of which depends on the original U to Si atomic proportion. In this case the combined density of the mixture of U_3Si_2 and the excess uranium is higher than that of U_3Si_2. The more excess uranium is present the higher the density of the fuel mixture [4]. Figure 1 shows the binary diagram of U-Si system, which explains the formation of the fuel mixture.

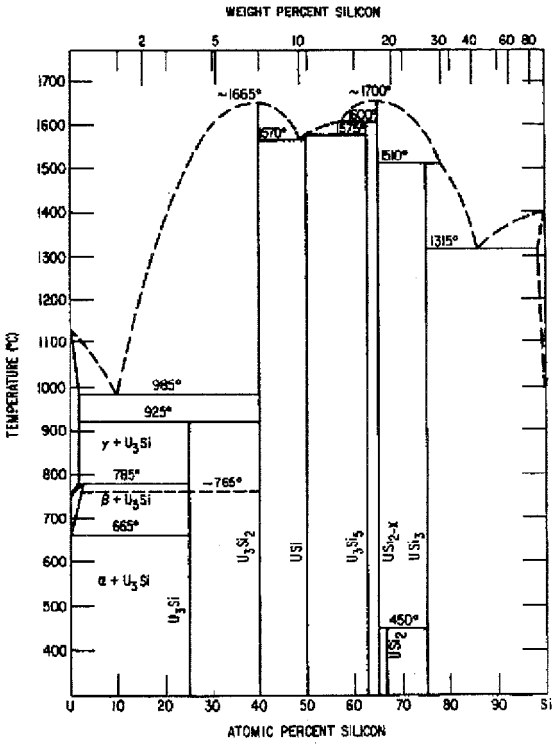


Figure 1. The binary diagram of U-Si system

The purpose of this experiment is to explore the possible use of the U_3Si_2 mixed with excess uranium described above for MTR-type dispersion fuel elements, hence achieving higher loading density than that achieved by stoichiometric U_3Si_2 fuel. It is commonly accepted that the presence of uranium in a fuel material results in bad swelling

behaviour of the fuel under irradiation, thus its presence in fuel is prevented. The present experiment was based on the assumption that the free uranium in the mixed fuel will react with the aluminum matrix to form an irradiation-stable fuel UAl_x during annealing of the fuel plate. This expectation was based on the studies of Bareis [5] and other researchers on the aluminum-uranium alloying reaction.

EXPERIMENTAL METHOD

The experiment was carried out by choosing 3.7 wt% of silicon which resembled the U_3Si atomic composition, thus departing far from U_3Si_2. The mixture was melted in an arc furnace under argon-controlled atmosphere and suddenly quenched to room temperature to inhibit the U_3Si to form.

The ingot obtained was then characterized by measuring its bulk density and its microstructure. Pulverisation by crushing and ball milling, followed by screening yielded the proper particle size distribution for fabrication.

Fuel plates were rolled with a standard procedure using the fuel powder and pure aluminum matrix material. A normal, and several extended annealing processes were carried out on hot-rolled fuel plates to allow the uranium-aluminum alloying reaction to take place.

RESULTS AND DISCUSSIONS

Mixed Fuel Ingot

The preparation of ingot containing 3.7 wt% Si was performed without any difficulty. Five flips (repeated melting by turning the ingot upside down) were conducted to insure homogeneous composition of U-Si throughout the ingot. The microstructure of the as-cast ingot obtained is shown in Figure 2. It can be seen that the excess uranium (dark image) forms veins between hard, shiny U_3Si_2 dendrites. The fine microstructure is likely to present a rather discontinuous path for aluminum diffusion into the uranium phase.

A separate work was therefore carried out to find a way to coarsen the microstructure of the as-cast ingot. Annealing temperature was chosen to be strictly in between peritectic and peritectoid temperatures of U_3Si_2 (see Figure 1, i.e., 985 and 925°C, respectively). In this bracketed temperature range there is unlikely any U_3Si to form during the annealing. As shown in Figure 3, the micrtrostructure has transformed into coarse spherical U_3Si_2 and more open free uranium. However, it has been observed that U_3Si did still form on the outer rim of the U_3Si_2 despite the strict temperature control applied. This more open microstructure may better expose excess uranium to aluminum matrix during alloying reaction.

The ingot density was found to be 15.5 MgU/m^3 when measured by immersion methods (picnometric method). The density was not found to change much after controlled annealing discussed above.

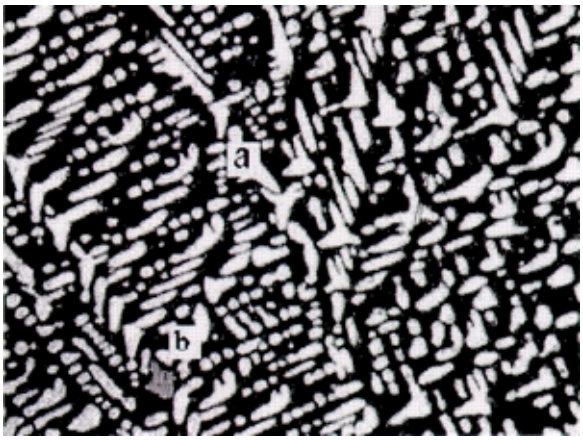


Figure 2. Microstructure of as-cast ingot, 3.7 wt% Si (resembling U_3Si_2) (a) the shiny dendrites of U_3Si_2 and (b) the dark uranium veins. (Magnification 300x)

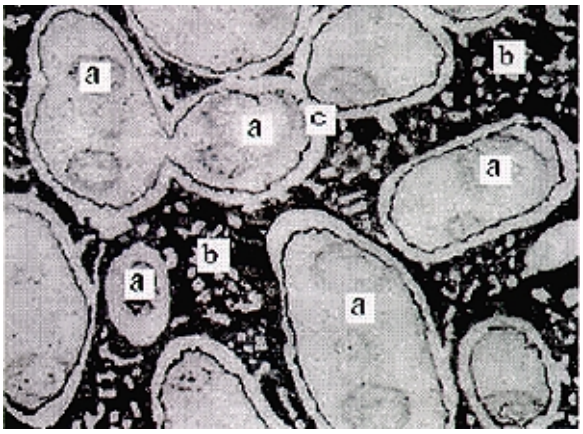


Figure 3. Microstructure of 12 hour-at 950°C-annealed ingot, 3.7 wt% Si (resembling U_3si) (a) the shiny dendrites of U_3Si_2, (b) the dark uranium veins, and (c) U_3Si rim (Magnification 300x)

Fuel Plates

The fuel plates were fabricated following standard picture and frame technique used for producing U_3Si_2-Al fuel plates. The standard fabrication procedure employs a repeated annealing and rolling of plates at temperature around 400°C for a total annealing time of about 2-3 hours.

Figure 4 shows the as-fabricated fuel plate containing meat of this mixed fuel and aluminum matrix. The picture shows that under the normal fabrication condition, the annealing performed did not change the appearance of dendritic U_3Si_2 in the fuel particle from its original appearance as shown in the as-cast ingot in Figure 2. This means that the normal fabrication condition is unable to transform or convert the free uranium into UAl_x. This is the result of the low temperature and short time being employed in the normal fabrication procedure.

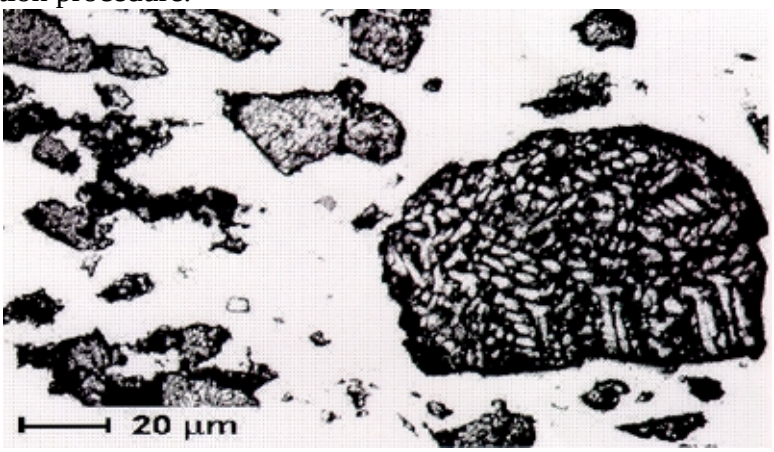


Figure 4. As-fabricated fuel meat using ground and milled as-cast ingot (3.7 wt% Si)

The key to achieving sufficient uranium-aluminum alloying reaction lies in choosing appropriate temperature and time as shown by Castleman [6] in Figure 5. To greatly enhance the alloying reaction the temperatures and times shown there all are beyond the normal temperature and time being employed in the fabrication of fuel plate. The rate effect is also shown in Figure 6.

Experimental annealing of the plates at varied higher temperatures for longer period of times revealed that the alloying reaction took place. Three representative results of these series of experimental annealing are shown in Figures 7 to 9.

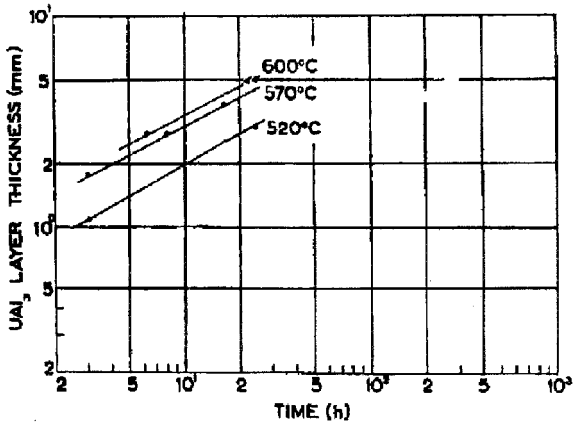


Figure 5. UAl_3 layer thickness growing between U-Al metal couple as a function of time and temperature (Castleman, 1960)

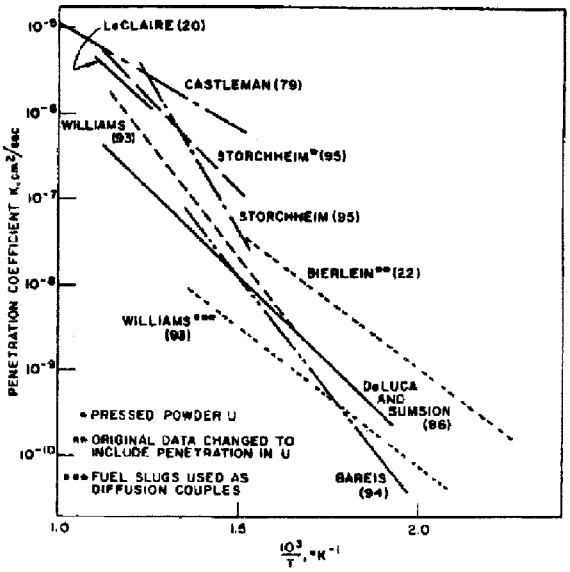


Figure 6. Arrhenius plot of U-Al diffusion system showing penetration coefficient vs. Temperature (DeLuca and Sumsion, 1957)

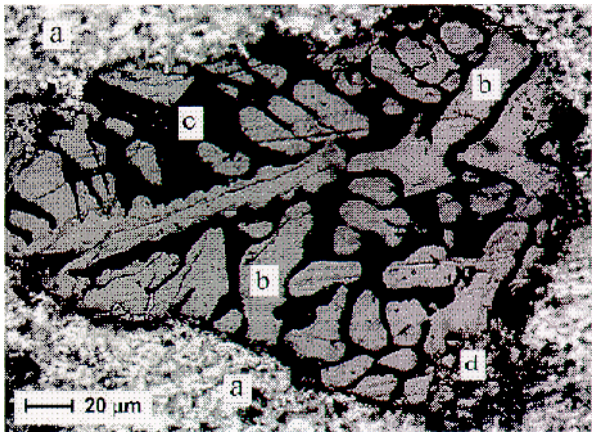


Figure 7. Section of fuel meat after annealing for 2 hours at 450°C.

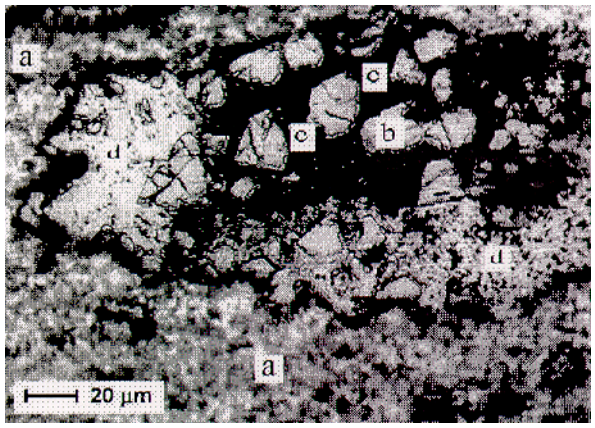


Figure 8. Section of fuel meat after annealing for 12 hours at 500°C

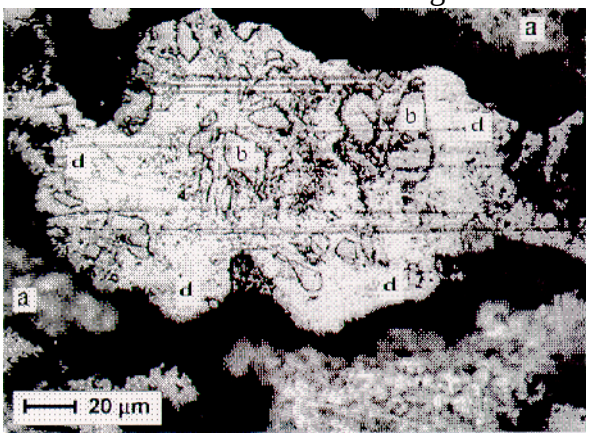


Figure 9. Section of fuel meat after annealing for 18 hours at 550°C

It can be shown clearly from Figures 7 to 9 that the temperature has to be much higher indeed than that used for the fabrication to affect the more complete conversion of the free uranium into uranium-aluminum alloy.

Following the lowest penetration coefficient curve of Williams (see Figure 6), the penetration coefficient can be estimated to be $K = 4.177\times10^{-4}e^{-7675.28/T}$, where K is the penetration coefficient as shown in Figure 6 and T is the absolute temperature.

According to Green [7] the diffusion of aluminum into uranium follows a parabolic relationship given in the form:

$$x^2 = K.t$$

where x is the penetration depth and t is the time. Combining K with the above parabolic expression one can compute the growth of the penetration depth with time.

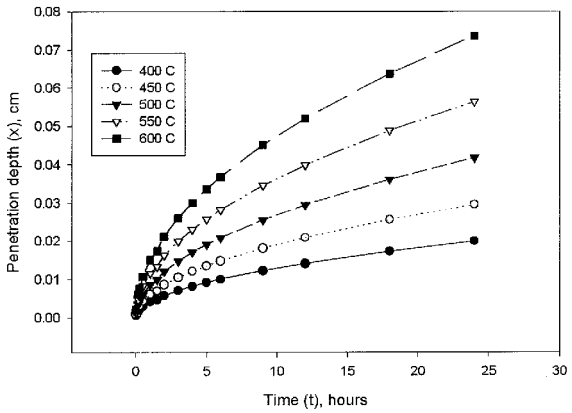
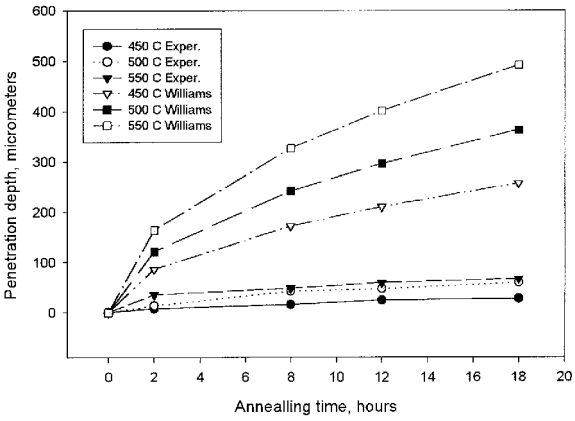


Figure 10. Penetration depth growth at different annealing times and temperatures

Taking the data of the depth of penetration at different times and temperatures in Figures 7 to 9, a set of graphs can be presented showing the comparison of the penetration depth growth of UAl_x. One clearly can see that the penetration depth in fuel mixture follows the parabolic correlation with time and temperature but with much lower growth rates than those obtained with the Williams correlation. This is due to the fact that the penetration of aluminum into the fuel particle bodies is masked by the present of dendrites of U_2Si_3. However, owing to the fact that the size of particles is normally much less than 100 micrometers, then this "incomplete" penetration can be acceptable. Besides, by transforming the dendrites into bigger aggregates, one can further expect to have better penetration depth growth for the same given time and temperature.



The alloying reaction will result in swelling of the fuel meat for the density of UAl_x is much lower than the combined density of the reacting uranium and aluminum. However, this can be overcome by the fact that the annealed plates will be cold-rolled to proper thickness.

Simple Calculation

The density of mixed fuel certainly depends on the amount of excess uranium content. The loading density depends further on volume loading percentage. In a simple calculation an estimate of fuel loading can be made.

$$U_{loading} = V_{loading} \times F_{density} \times U_{content}$$

where $U_{loading}$, $V_{loading}$, $F_{density}$, and $U_{content}$ are uranium-loading density (MgU/m^3) in the meat, the volume percentage loading of fuel in the meat, true density of fuel (Mg/m^3), and the weight percentage of U in the mixed fuel, respectively.

For example: a 45-volume loading (this is a normal practice) of a mixed fuel having a true density of 15.5 Mg/m^3 and 96.7 wt% uranium in it, will result in:

$U_{loading} = 0.45 \times 15.5 = 6.74\ MgU/m^3$.

Keeping the volume loading to its given figure, one can only increase the uranium content in the mixed fuel to a value limited by the available amount (for complete reaction) of aluminum matrix. The uranium content has a double effect on the uranium loading increase for it also directly increases the true density.

CONCLUSIONS

The experiment has been successful in showing that the mixed fuel containing U_3Si_2 and free uranium can be significantly transformed into a mixture of U_3Si_2 and UAl_x, the latter being the result of U-Al alloying reaction. The transformation rate however is observed to be rather slow owing to the fact that the U_3Si_2 dendrites mask the free uranium veins from attack of aluminum matrix.

A careful annealing of as-cast ingot at a temperature between the peritectic and peritectoid temperatures may be the solution to enhance the alloying reaction by means of coarsening the microstructure of the as-cast ingot. Further work in this direction still has to be performed.

The temperatures and times used to bring the transformation to completion are still workable but result in an additional cost of extending annealing temperature and time.

The swelling implication of such a transformation is expected to be removed by applying a cold rolling operation to bring the plate to its proper dimension.

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